

## THE IDEAL CERAMIC FIBER/OXIDE MATRIX COMPOSITE : HOW TO CONCILIATE ANTAGONIST PHYSICAL AND CHEMICAL REQUIREMENTS ?

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**Abstract :** Starting with a short historical introduction, this paper deals with the search for the best materials to be used in ceramic composites. The reinforcement and oxide matrix must satisfy multiple - and often antagonist - requirements in terms of physical (failure resistance, damage tolerance) and chemical (thermal stability, corrosion resistance) properties. The best compromise is obtained by "control" of the interface or, if none forms "naturally", by specific coatings. We will illustrate the choice process with some examples (among which Lithium AluminoSilicate (LAS) composites) showing how "out of factory" short-term (airspace or military applications) and long term (civil air transportation, energy plants) specifications lead to different choices, the latter demanding careful assessment of corrosion issues.

**Résumé :** Le composite céramique idéal à matrice oxyde, ou comment concilier des critères physiques et chimiques contradictoires. A partir d'une brève histoire des composites céramiques, après avoir défini les contraintes physiques et chimiques que doivent satisfaire idéalement le renfort et sa matrice céramique oxyde, nous discutons, au travers de quelques exemples dont les Lithium Alumino-Silicates (LAS) des critères contradictoires, physiques et chimiques, de sélection des 3 matériaux constitutifs d'un composite: les fibres, la matrice et la zone interfaciale fibre-matrice, que cette dernière soit créée "naturellement" lors de la synthèse ou bien volontairement par un dépôt spécifique. Les implications résultant du choix des matériaux aussi bien sur le plan des propriétés mécaniques (résistance à la rupture, tolérance aux dommages) que sur celui des propriétés chimiques (stabilité thermique et chimique, tenue à la corrosion) sont analysées afin d'explicitier les stratégies menant à un compromis optimal aussi bien pour les caractéristiques "sortie de fabrication" que pour celles prenant en compte des utilisations "courtes" (domaine spatial ou militaire) ou "longues" (aviation civile, énergie) pour lesquelles les problèmes de tenue à la corrosion deviennent déterminants.

## 1. SOME HISTORY

Let us recall a few concepts before commenting the physical and chemical requirements of a ceramic composite. First, a ceramic can be defined as a sintered material which matter, inorganic and obtained before complete fusion, possesses ionic-covalent chemical bonds. Unlike collective metal bonds, such “binary” bonds can not withstand local efforts exceeding the bond strength. The failure propagation from bond to bond is characteristic of a quasi-instantaneous and fragile rupture demanding very little energy [1]. Besides, ceramics being a collection of grains (and flaws), each one is unique and most properties, including the mechanical ones, have a statistical behavior [2]. The strength of ionic-covalent bonds makes ceramics very hard materials but necessitates high temperature sintering. In ancient time, potters soon explored two antagonist routes to find an acceptable compromise :

- i) obtain the hardest ceramics they could.
- ii) avoid cracks propagation.

The first route led to low-porosity ceramics with strong “non-shearing” covalent bonds in all directions, like typically traditional porcelains [3] ; the second route concerns multiphased materials like stoneware and terra cotta where a secondary phase or pores deflect and slow down crack propagation.

In spite of the common belief, long-fiber reinforced composites are not a modern days invention. For instance, long mullite needles imprison the glassy second phase in the highest quality porcelains, which is the reason why they do not deform at high temperature, in spite of a high liquid phase proportion [3].

To the best of our knowledge, the oldest true composite was “designed” in Corsica during Iron Age using natural asbestos fibers from the North-East part of the island [4,5]. Excavations from a number of post Middle-Age sites confirmed the importance of this type of production. The first academic study on this kind of long fiber reinforced composites is due to Alexandre Brongniart (the author of a famous "Traité sur la porcelaine" and Director of Manufacture de Sèvres) and dates back to 1838-39. Asbestos-reinforced ceramics were still produced in Corsica as late as in the 1940': They used 3 to 1 mixtures of earth (either red, black or white clay according to the village) and asbestos. The fibers were split (but not torn) with a pebble, mixed with the raw hand- or foot-worked clay paste and subsequently fired at low temperature (~600-700°C) in the village kiln. This was used to make light, tough and porous (tightness resulted from burnt fat, honey and milk residues) cooking recipients or utensils (ovens, grills, vessels, etc). Most often black, these recipients were perfectly suited to resist the thermal and mechanical shocking of domestic use. Ancient potters had soon understood that the best fiber and matrix materials did not necessarily give the best composite because the preservation and incorporation of the former in the latter was a key parameter that sometimes required a compromise.

This paper does not intend to be exhaustive but, rather, to discuss on practical examples, how designing a composite is a matter of choice. Crystallo-chemistry indeed makes the chemical and physical properties of composites inter-dependant, which means physical and chemical specifications can be antagonist.

## 2. THE IDEAL COMPOSITE

In a composite, a reinforcement (most often fibrous) providing high mechanical properties is embedded in a damage protecting matrix ensuring chemical protection of the fibers, load transfer and the overall shape of the parts. The so called “composite effect” stems from the exceptional

mechanical properties of the fibers (carbon, SiC, mullite, etc.) that are used. Some physical and chemical parameters have obvious importance but we shall see that additional implicit criteria can play a paramount role ; their non-consideration often turned into a disaster. The first one of these is the homogeneity and quasi-absence of flaws in the fibers. This ensues from their small diameter and a synthesis from usually hybrid liquid precursors incorporating mineral and "organic" hydrogen-rich groups [6-8]. The progressive removal process of highly diffusive hydrogen results in a "soft" conversion to a ceramic. The transformation can be stopped in a optimal intermediary nanocrystalline state combining a high bond density (a characteristic of crystals) with a high homogeneity (a characteristic of the grain boundary- and second phase-free amorphous state) [6,8-10] and limited skin-core gradients.

### 2.1. The ideal interface

Composite structures exhibit a non-fragile dissipative mode of failure starting from materials that are intrinsically fragile [1]. Not only must the fiber-matrix bond be strong enough for this remarkable transformation to occur (load transfer and energy dissipation by fiber-matrix sliding) but it must remain sufficiently weak to support cleavage and therefore act as a "mechanical fuse" (crack entrapment) [11]. Indeed, cracks propagate in ceramics only when the crack tip energy reaches a threshold that corresponds to the bond failure energy. If the fiber-matrix bonds are weak or the interface cleaves easily, the crack tip surface is multiplied (for instance by a fiber circumference) and propagation stops since the stress intensity falls instantaneously below the above-mentioned threshold. Note other elements than the fibers such as hard particles or pores can produce the same effect. We shall see further that the thermal expansion of the different phases, including the fiber-matrix interphases, but also their structural anisotropy (cleavage determining factor) are important parameters.

### 2.2. How to maximize the mechanical strength

One of the advantages sought when incorporating reinforcements is their excellent mechanical resistance. We already mentioned how this property ensues from their high homogeneity (absence of grain boundaries and nano-crystals) and synthesis via liquid precursors transformation (polymers, sol-gel, etc...) [7,8] but it is also a consequence of their small dimension (typical fiber diameter is ~8-15  $\mu\text{m}$ ) [6], which maximizes the surface to bulk ratio of matter and, thus, the overall quality of the ceramic (flaws or attracted and eliminated close to the surface under the effect of the diffusion gradients [2]). It is also very important that the strong bonds density be maximal whatever the direction and this disqualifies amorphous and low density crystalline materials.

There is thus a first set of contradictory criteria : amorphous phases are more homogeneous than their crystalline counterparts but possess a lower density of bonds. A nanocrystalline structure then appears as a good compromise but might not offer a good thermo-chemical stability (smaller grains mean extended interfaces and, thus, higher reactivity) [10].

### 2.3. How to resist thermal cycling

Ceramic composites experiment large amplitude thermal cycling. Low expansion materials are therefore desired but what are the cristallochemistry criteria responsible for a low thermal expansion ? This feature originates from the individual expansion of chemical bonds chains in all space directions and is most specifically dependent on the deepness and anharmonicity of the potential wells [12,13]. The deeper the well, the further the bond dissociation threshold (the fusion temperature) and the lower the anharmonicity.

Glassy silicates expansion is predictable by simple linear combination of the components expansion weighed by the respective proportion in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, CaO, etc. [14]. A number of refractory ceramics have a thermal expansion in the range 40 to 80 10<sup>-7</sup> /°C when that of metals is usually above 100 10<sup>-7</sup> /°C. Anisotropy leads to a direction-dependent expansion [13] but this drawback disappears in polycrystalline ceramics where grains are distributed at random.

Some materials exhibit almost nil or, even, negative expansion over large temperature ranges. This happens when ionocovalent moieties (for instance XO<sub>4</sub> tetrahedra in silicates and phosphates) organize in open frameworks where rotations or deformations of the moieties compensate for the bonds thermal expansion [13-19]. There is still a threshold temperature at which a phase transition or, if the material was originally amorphous, a crystallization, suddenly takes up the postponed macroscopic dilatation. Quartz α-β transition is a well-known example. Glassy silica is another. Some alumino- (β-eucryptite, spodumene [18]) or phospho-silicates (Nasicon [15-17]) exhibit this behavior in the range 500-1000°C, which makes them useful for thermostructural applications (aeronautics, turbines or fusion reactors). Unfortunately, the benefit open structures provide from the thermal expansion point of view is accompanied by easier (low activation energy) and faster (high prefactor) ionic diffusions [20-25]. The most ionic (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, ...) [21,22] or mobile (protons) [20,23,25] species induce high exchange-conduction properties which sometimes favour the formation of a good fiber-matrix interface (reaction with some SiC fibers [25,26]) but can also dramatically speed up corrosion mechanisms [25].

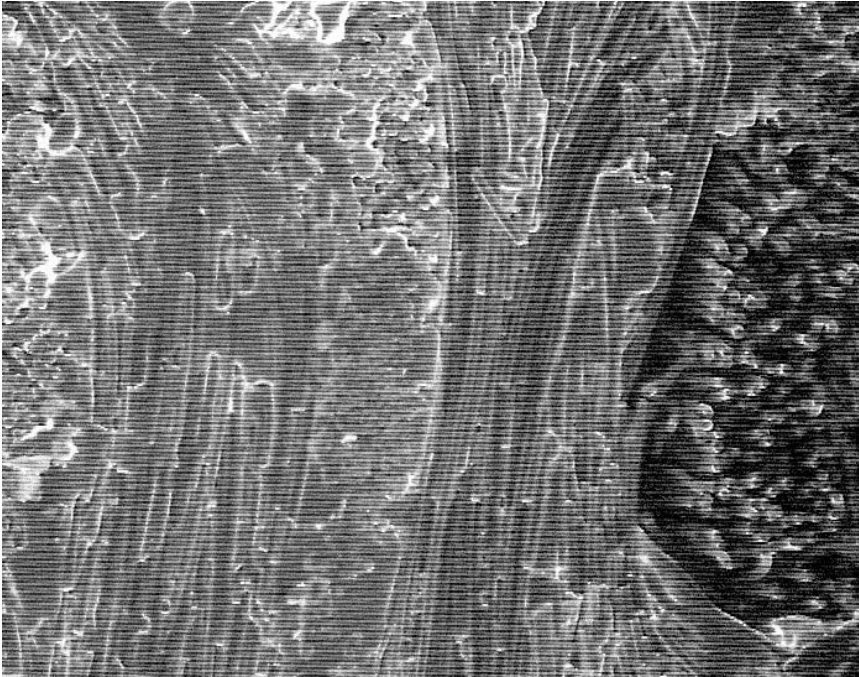
Note that the long distance coulombian interactions associated with ferroelectricity can stabilize open frameworks but the structural rearrangement will be all the more brutal that the stabilized temperature range is wide. Besides, this stabilization is very sensitive to any doping.

Lastly, iono-covalent bonds have very asymmetrical potential wells, which makes them more resistant in compression than in tension. It is consequently mandatory that the weaker material (the polycrystalline matrix ; porous in 3D-reinforced composites) be compressed by the stronger (the reinforcement). This imposes the thermal expansion of the matrix to be at least 20 to 30% lower than that of the reinforcements, which usually occurs in materials with open frameworks.

#### 2.4. How to protect the fibers from aggressions

During composites elaboration, the matrix must accommodate the desired composite geometry, respect the fibrous reinforcement orientation and the fibers pristine state [27]. In the working conditions, the matrix should also protect the fibers against all physical and chemical aggressions. Moreover, in a number of applications, the fibers must withstand stresses in given directions, according to the sequence of layers stacking (0<sup>d</sup>, 45<sup>d</sup>, 90<sup>d</sup>, etc.). Whenever possible, bonding must be favored in the stacking direction or, alternatively, preforms, mats and fabrics must be used. On account of ceramics stiffness, only small diameter fibers, typically between 5 and 15 μm according to Young's modulus [6], can be used. They are in the form of threaded yarns, each of them including hundreds to thousands of fibers. The matrix incorporation in such tight structures where inter-yarns and inter-fibers intervals do not exceed respectively ~50-500 μm and one tenth of the typical fiber diameter (*Figure 1*, ~1μm or less) is a very difficult operation that requires either gaseous (but the method is slow, not adapted to thick parts and restricted to "simple" compositions) or liquid/ultrafine powder precursors [28-31]. The precursor to ceramic conversion rate obviously remains well below unity with gaseous precursors. With liquid precursor like submicronic powder slips [30-32] or polymer and sol-gel precursors [28,32-34], this ratio is better but never exceeds 0.5. The consequence is a strong discrepancy between the volumes initially and ultimately filled with matter. Besides, the fibrous structure being a geometric invariant (*Figure 2*), different strategies had to be developed to obtain "net shape sintering" [8,9,30,32-35]) or, alternatively, limit shrinkage to specific directions (the "pre-preg route" [34,35]). Lastly, because pores and cracks limit the

protection provided by the matrix, standard and self-healing barriers where deposited on composites surfaces [11,36-38], following initial work on C/C composites protection [39].



**Figure 1.** The filling of the inter-fiber space in the preform yarns requires matter precursors to reach and penetrate (sub-)micronic interstices and often results in porosity ; see right part of the figure : carbon fibers with diameter  $< 10 \mu\text{m}$  and interstices of  $\sim 0.5 \mu\text{m}$ .

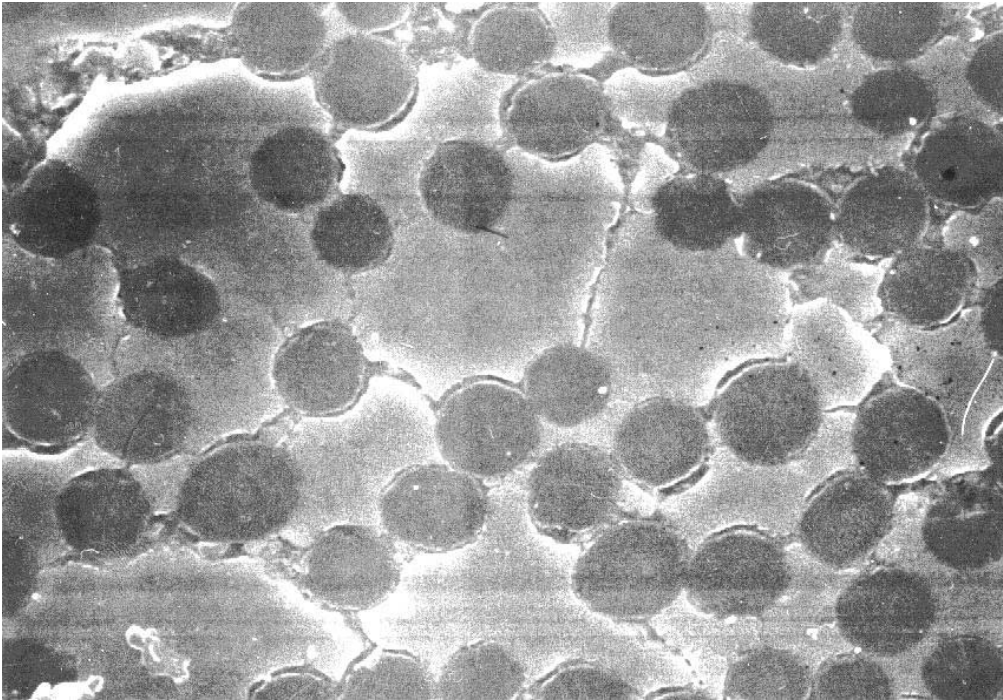
### 3. THE CHOICE CRITERIA FOR A GOOD FIBER-MATRIX COUPLE : CASE STUDIES

The materials incorporated in long fibers reinforced composites must comply with some mechanical, chemical and economical criteria.

#### 3.1. Mechanical criteria

Choice criteria are specific to each element and directly related to composition (failure resistance at the working temperature, Young's modulus and thermal expansion) or the process (diameter, volume fraction and fibers disposition). To this adds the fiber-matrix interface nature (debonding threshold, sliding stress, stability), which defines the work of failure and the dissipative character [40]. The matrix having a mechanical resistance 3 to 10 times lower, it should have a thermal expansion only 70 to 80% that of the fibers so that they support the strain. This is why the Pyrex<sup>TM</sup> glass matrices that were used in the first attempts to design long fiber-reinforced composites were soon replaced by refractory lithium aluminosilicates (LAS) glasses and glass ceramics. Besides, LAS processing conditions had already been defined for previous applications [41] and it was anticipated that their mechanical resistance could be improved by crystallization of the glassy state [42].

All in all, the more thermal expansion differs with that of the fibers ( $\sim 30 \cdot 10^{-7} / ^\circ\text{C}$ ), the wider the matrix compression temperature domain – which prevents cracking – and the better the mechanics of the composite. The resistance should then approach the theoretical maximum obtained when multiplying the fiber length (in the solicitation direction) by the fibers stress to failure.



**Figure 2.** Example of the oxide matrix cracking resulting from densification in a geometrically invariant fibrous preform.

### 3.2. Chemical and processing criteria

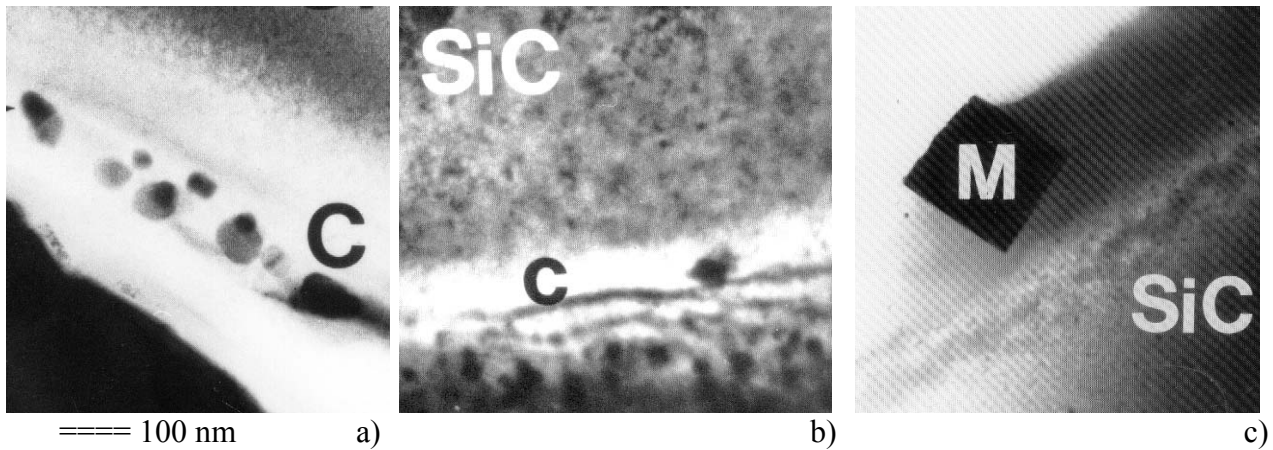
Such criteria concern processing (matter must be brought in between the fibers efficiently) and control of the fiber-matrix reaction to avoid fiber-matrix adhesion over the whole working range (temperature and service time). Available in the form of amorphous precursor (glass powder), LAS compositions offered the advantage to be "injectable" in the molten state at temperatures compatible with graphite molds use. Besides, the fine powders were stable, non toxic, absorbed little moisture and could be melt and injected at low viscosity with a volume "densification" yield close to one. Lastly, LAS matrices alkaline ions happened to react with the carbon and oxygen-rich first generation SiC fibers, especially the NLM Nicalon<sup>TM</sup> grade (Nippon Carbon, Japan), to produce a sliding carbon interface [41].

### 3.3. Economic criteria

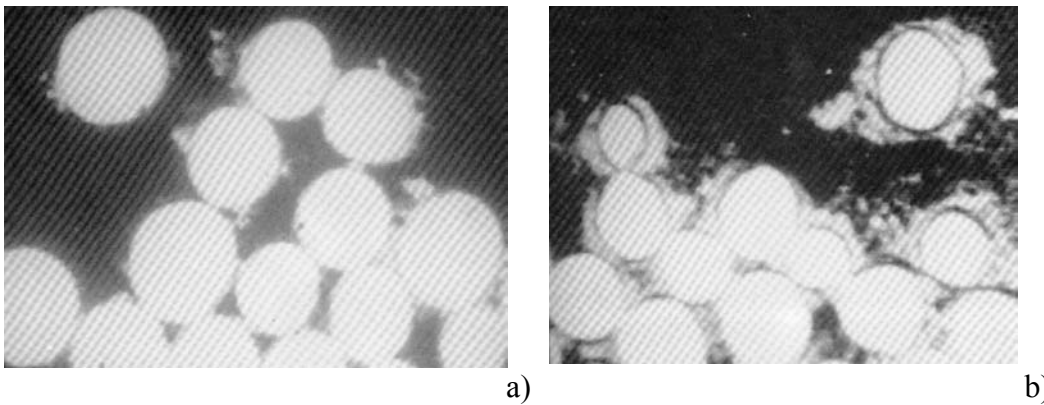
We will not discuss economic factors extensively but let us recall that fibers from grades that require either specific thermal annealing or CVD deposits, are much more expensive compared to "standard" ceramic fibers. Another parameter that can not be neglected is the additional price of working in controlled atmospheres (water, oxygen, etc.) with materials that are potentially toxic or flammable.

### 3.4. Good reasons for a bad choice : LAS composites

When many "serious" laboratories opted for the SiC/LAS (or variants) solution, data on this couple chemical instability in combustion atmospheres were already available in the literature [43-49]. We shall try to learn from their "mistake" and propose better strategies for the future.



**Figure 3.** TEM microphotographs of the interfaces between NLM202 Nicalon<sup>TM</sup> (Nippon Carbon, Japon) SiC fibers and a) LAS, b) CAS or c) “glassy” mullite (the black square is a mullite crystal) matrices. Note a carbon interphase (in white) is present in the first two cases only ; the SiC fiber appears at the top (a,b) or at the bottom ©, with authorization from Editions de Physique, © 1993, *J. Physique C-7*, 1937, *ibidem* 1941.



**Figure 4.** Cross section Energy Dispersive X-ray spectroscopy (EDX) images of silicon concentration in Hot-pressed NLM202 Nicalon<sup>TM</sup> SiC fibers ( $\phi \sim 12 \mu\text{m}$ ) -  $\text{Al}_2\text{TiO}_5$  matrix composites ; a) Hot pressing temperature :  $1270^\circ\text{C}$  ; b)  $1350^\circ\text{C}$ , note the important level of Si diffusion, with authorization from AMAC, Proc. 8<sup>ème</sup> Journées Nationales sur les Composites, JNC’8, 16-18 novembre 1992, Palaiseau, O. Allix, J.P. Favre & P. Ladevèze eds., AMAC, Paris (1992) p. 253-264).

LAS-based glass ceramics present some interesting properties. First, the several varieties of lithium aluminosilicates ( $\beta$ -eucryptite,  $\beta$ -spodumene, etc...) all derive from silica structures (quartz, keatite, cristobalite,...) through replacement of some silicon ions ( $\text{Si}^{4+}$ ) by aluminum ions ( $\text{Al}^{3+}$ ) and charge compensation by lithium ( $\text{Li}^+$ ) or other ( $\text{Mg}^{2+}$ ,  $\text{P}^{5+}$ , etc.) ions. These substitutions (in solid solutions between  $\text{LiAlSiO}_4$  and  $\text{LiAlSi}_2\text{O}_6$  and their  $\text{Mg}^{++}$ ,  $\text{Ti}^{4+}$ ,  $\text{P}^{5+}$ -containing homologues) destroy part of the Si-O-Si bridges, which lowers the fusion temperatures and viscosities and, thus, makes injection of molten glass possible in the  $1200\text{-}1450^\circ\text{C}$  range [33,41,50]. Besides, substitutions induce some disordering and block phase transitions. In the resulting "open" structures, bond angles deformation can accommodate bonds thermal expansion and the resulting macroscopic expansion is limited (and even negative in some directions) in a large temperature

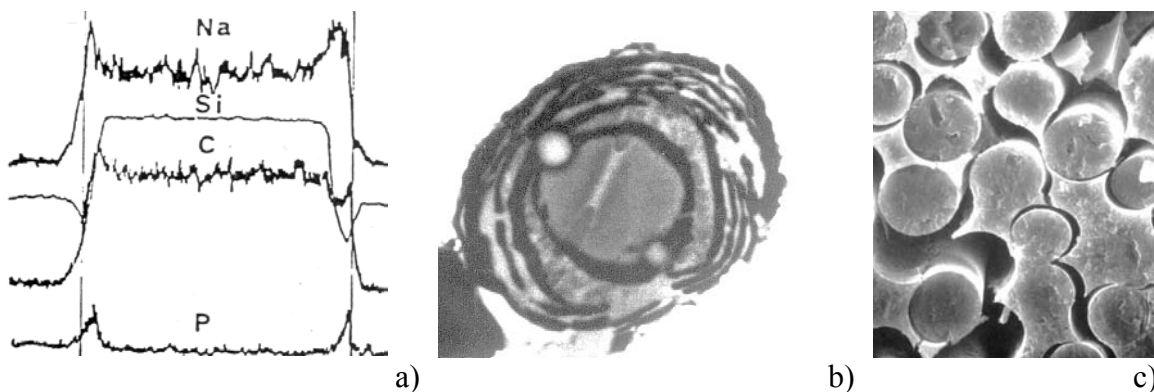
range [17,18]. Lastly, LAS easily gives glass ceramics, with the possibility to maintain the crystallite size below a certain value in case optical transparency is required (telescopes mirrors, cooking plates, etc...)

The Nicalon<sup>TM</sup> SiC fiber/LAS matrix association immediately seemed to be very attractive and very good mechanical properties were actually obtained [33,41,50]. The carbon interface formed after LAS matrix injection proved to be a very efficient mechanical fuse (*Figure 3*). Many studies soon reported on the characterization of this interface but its formation mechanism was elucidated only when its comprehension became crucial to adjust the interface conductivity, in view of obtaining stealthy missile materials in the microwave domain [51,52]. Two important phenomena could be isolated by the comparison of diffusion mechanisms from NLM202 Nicalon<sup>TM</sup> fibers to silica-free matrices ( $\text{Al}_2\text{TiO}_5$  [52,53]) and matrices either containing (celsian (BAS), anorthite (CAS), Nasicon ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ) [26,51-54]) or lacking (mullite ( $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ) [29]) alkaline/earth-alkaline elements :

- i) silicon exo-diffusion from the fiber to the matrix (*Figure 4*)
- ii) some sodium diffusion in the fiber, the subsequent destabilization of the oxycarbide and SiC phases giving the carbon interface. This diffusion was very sensitive to Nicalon<sup>TM</sup> textural and compositional heterogeneities [25,51] (*Figure 5*).

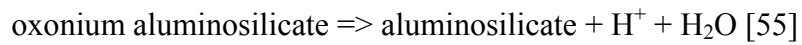
### 3.5. The corrosion issue or “how could all anticipated assets result in disappointing composites ?”

The first designed composites were intended to work in "ultra clean" atmospheres (satellites) or for very short service times (rockets, missiles). Their fast degradation could be counteracted by oversizing but specifications for newer applications such as military and civil engines, filters in domestic waste treatment plants, coal gasification, etc... imposed more severe conditions (corrosion cycles during turbines warming/cooling, aggravated by marine corrosion on aircraft-carriers) and much longer service times, as high as tens of thousands of hours ! Oxidation and corrosion induced by the atmosphere (water,  $\text{NO}_x$ , protons,  $\text{Na}^+$ ,  $\text{Cl}^-$ ) and kerosene impurities (Na sulfates, vanadium) took a prime importance [25] in the case of open structures, where ions diffused/exchanged very fast [20-22]. Many publications from the 1950' and 60' already pointed  $\text{Li}^+/\text{H}^+$  easy substitutions in LAS [43-46] and more or less similar structures [47-49]. The replacement of some  $\text{Li}^+$  ions by protons had two main consequences :

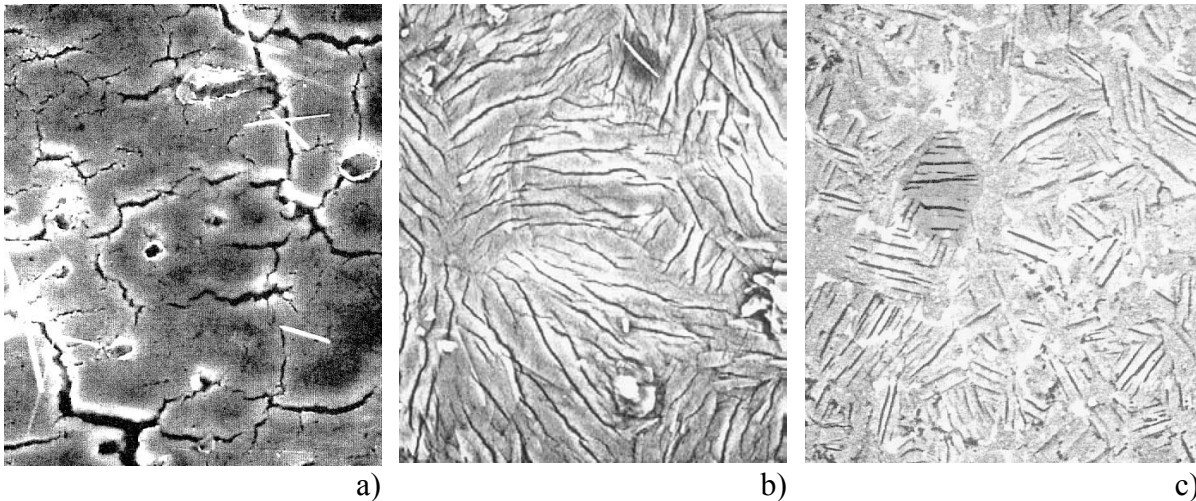


**Figure 5.** Observation of NLM 202 Nicalon<sup>TM</sup> SiC fibers embedded in sodium-rich matrices: a) Na, Si, C and P EDX-based concentration profiles through the fiber section. Note the sodium and phosphore-enriched carbon interface that forms at the fiber-matrix interface ; b) The reaction sometimes reveals reactivity (in other words composition) heterogeneities; c) The good fiber-matrix debonding of this type of interfaces shows after flexion testing on the polished cross section of SiC-NASICON composites.

- a reduction of the thermal stability domain when protons diffused from the original lithium site, thus provoking volume changes, stresses and, even macroscopic cracking (*Figure 6*).
- a combination of the protons with oxygen ions via the following reaction :



This reaction gave iono-covalent ceramics stable up to 900°C, which is remarkable for protonated compounds, but that suddenly collapsed when protons started diffusing. Large scale testing of these ceramics was carried out in the 1970' (monoliths were tested in turbines/burner rigs) and showed their rapid degradation [45,46]. Surprisingly, this was later (un-?)voluntarily ignored.

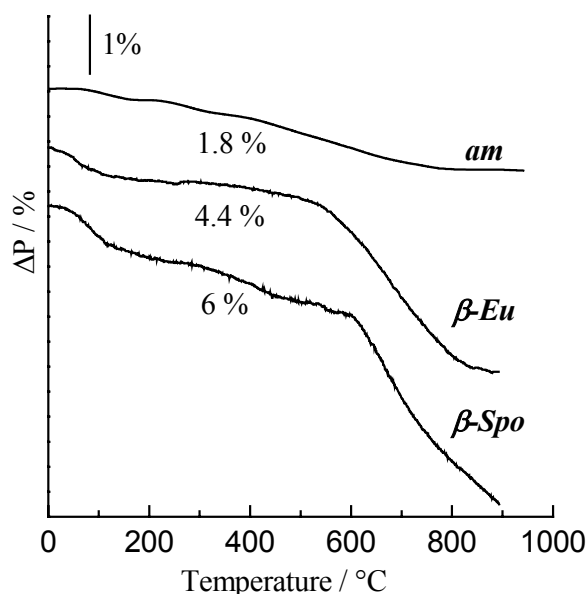


**Figure 6.** Cross sectional micrographs showing the cracks appearing after 0.5h in concentrated boiling  $\text{H}_2\text{SO}_4$  acid in (a) amorphous, (c) crystalline  $\beta$ -spodumene or (b) intermediate LAS samples. The treatment simulates the protonic attack during a turbine combustion cycle.

#### 4. THE SEARCH FOR A COMPROMISE

*Figure 6* compares polished cross-sections of either amorphous, crystalline or intermediate LAS monoliths after immersion in boiling sulfuric acid. The fast  $\text{Li}^+/\text{H}^+$  ionic exchange is intended to simulate the attack of condensed molten salts in the heating and cooling stages of aerospace turbines working cycles [23]. The contraction of LAS unit cells induce grain cracking-cleavage. Two types of solutions were explored, both aiming, although this was never explicitly stated, at blocking ionic diffusion and, consequently, reducing degradation phenomena :

- The first one limited diffusion topologically by favoring amorphous structures (diffusion path increases and stability increases, as seen in *Figure 7* [23]). In the crystalline counterpart having same composition, cracking is irregular and has an almost fractal behavior. Crystalline LAS structures possess 1D diffusion pathways for  $\text{Li}^+$  ions that disconnect with amorphisation. The observed cracks give a macroscopic image of the canals nanometric connectivity. Intermediate state materials sometimes offer the best "compromise". The mass loss shown in *Figure 7* illustrates how crystalline LAS (either  $\beta$ -eucryptite or  $\beta$ -spodumene) are more reactive.



**Figure 7.** Mass loss of lithium aluminosilicates exchanged in concentrated boiling  $H_2SO_4$ . The loss results from protons substituting part of lithium ions in amorphous (*am*),  $\beta$ -eucryptite ( $\beta$ -*Eu*) and  $\beta$ -spodumene ( $\beta$ -*Spo*) LAS monoliths. The monolith will be all the more stable that its mass loss will be limited (no proton incorporation).

- The second option consisted in substituting lithium by bigger ions (calcium and barium giving respectively CAS and BAS feldspar tecto-silicates [54,56,57]), to slow down diffusion and reactivity, or to incorporate ions like  $Mg^{2+}$  to obtain cordierite-like materials where the network of diffusion canals disappears [33]. Other problems aroused because a lamellar silicate forms predominantly rather than the wanted tecto-silicate. The resultant anisotropy is detrimental to mechanical properties but partial substitution by strontium, specific synthesis routes or doping limit this drawback [56].

#### 4.1. Alternative interfaces to carbon

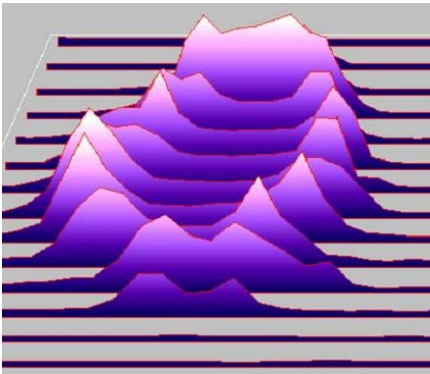
The progress toward more stable fibers and matrices stopped the spontaneous apparition of a carbon interface that resulted from SiC fibers destabilization by conjugated alkaline attack of the oxycarbide phase and outward diffusion of silica [26,52,53]. Very little attention is paid in the literature to the latter phenomenon and, more generally, to all issues regarding inter-diffusion of elements initially present in two materials. Alternative materials to this carbon interface (unstable in oxygen above 700°C anyway) had to be looked for : first BN (isotypic to graphite) [11,58] and then highly refractory materials [59]. The strategies consisted in :

- replacing the interface with an "inert" interphase that did not react with the fiber (either because of its intrinsic refractoriness (zirconia [8,60]) or because of a sintering temperature low enough not to provoke any reaction [27,35])
- using interfaces becoming porous, multi-cracked or lamellar [60,61] or, even, temporary material leaving a void after controlled elimination [62]. These cases are addressed in this issue [63] or have been presented elsewhere [64].

We will not elaborate on all solutions and will rather focus on the example of BN, as it perfectly illustrates the difficulties of simultaneously fulfilling physical and chemical requirements.

Boron nitride (BN) presents the same cristallochemical forms as amorphous carbon, diamond (cubic BN) and graphite (hexagonal BN). The cracking or cleavage of non-cubic phases is very easy and make them good interface compounds. Besides, BN oxidation starts about 200 degrees after that of carbon interfaces (which provokes composites degradation around 650-700°C). Yet, this retarded oxidation produces  $B_2O_3$  oxide, which reacts with all oxides at temperatures lower than that of carbon combustion. Besides,  $B_2O_3$  is soluble in hot water and its direct reaction with oxide matrices produces very aggressive fluxes, which strengthen the fiber matrix interface. *Figure 8* shows the example of the reaction between BN coating and a SiC/Si<sub>3</sub>N<sub>4</sub> fiber, in a BAS matrix [65].

All in all, even the self-healing interfaces obtained by complex combinations of C and BN layers [11] for short term applications do not comply with the lifetimes specified for future anti-pollution norms in civil air transportation.



**Figure 8.** Raman imaging of the BN interphase reaction with a mixed SiC-Si<sub>3</sub>N<sub>4</sub> fiber (section  $\sim 14 \times 8 \mu\text{m}^2$ ) and the BAS matrix (after ref. [65]) : BN deposit was initially  $0.4 \mu\text{m}$  thick but reacted over several micrometers, with authorization from the American Ceramic Society © 2002, *Ceram. Trans.* 135, 205).

#### 4.2. The "all-oxide" composites

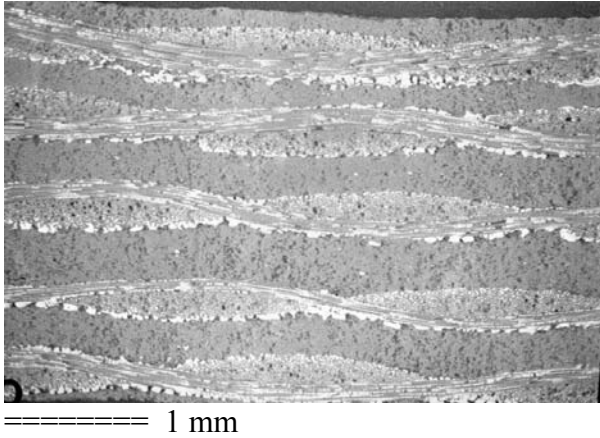
The materials that are traditionally used for short time applications in “clean” atmospheres would not resist the corrosive turbines atmospheres and much more stable materials must be used : alumina, mullite, zirconia, ... (see review papers [63,64]). Different options were explored :

- i) one was to keep SiC/oxide associations thanks to appropriately designed interphases [8,9,52,53].
- ii) the other was to switch to "all-oxide" systems (*Figure 9*) [60]. Intermediate expansion fibers (mullite for instance) and good resistance matrices like alumina or mullite are the most promising components from a mechanical point of view but it is crucial to preserve the nanometric state of the fibers while preventing strong fiber-matrix adhesion. Good results were obtained with some specific interfaces, especially those made in zirconia [60-64] and particularly through the sol-gel route [8,27,60,63,64].

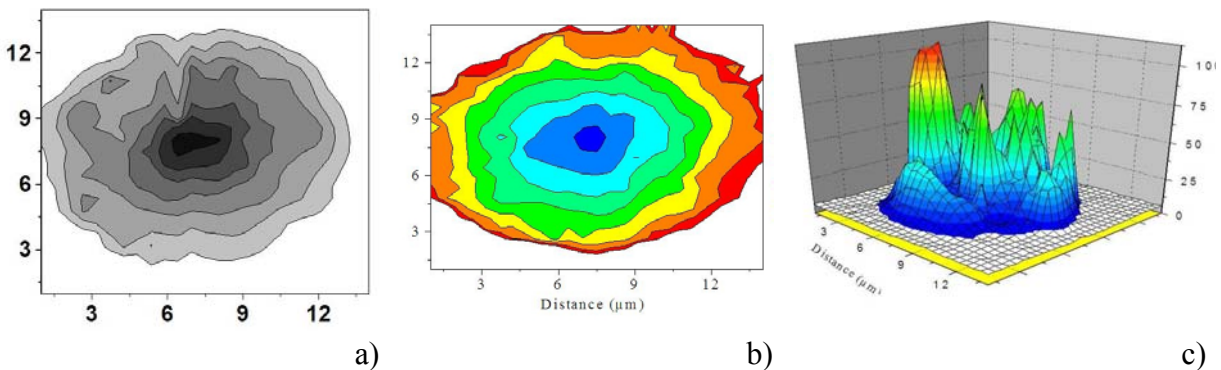
#### 4.3. The fibers

Just like for matrices, the fiber materials offering the best compromise between mechanics and chemical stability have homogeneous and nanometric structures [6]. The reactivity of such materials in corrosive atmospheres is very dependant on composition gradients and grain size distribution, for the characterization of which specific non-destructive methods had to be developed

[10,66,67]. Transmission Electronic Microscopy (TEM, *Figure 3*) gave data but at very high time and technological costs [6]. *Figure 10* shows Raman-based images of carbon second phase distribution (*Figure 10a*) and aromaticity (which variations are the consequence of the fiber "firing gradient"; *Figure 10b*) in a SiC fiber. As a grain growth inhibitor, this phase contributes to the good mechanics of the fibers but its high reactivity reduces the stability in aggressive atmospheres [66,67].



**Figure 9.** Oxide/oxide composite associating layers of alumina fibers (Almax™) with a porous zirconia interphase and a mullite matrix.



**Figure 10.** Raman images of SA3™ SiC fibers (Ube Industry, Japon) showing a) the heterogeneity of carbon second phase (max. concentration at core) and b) the carbon aromaticity (peaking at core). Rayleigh imaging shows the heterogeneities impact on corrosion with alkaline salts (c) ; with authorization from Wiley (C) 2003, *Spectroscopy Europe* 15, 8).

## 5. CONCLUSIONS

This paper recapitulates the various strategies followed in the last two decades to develop new oxide matrix composites. The aim has always been to find the best compromise between mechanical and chemical requirements, the most obvious property to look for being good thermomechanics. The nature and structural organization of the chemical bonds must be taken in consideration because of their direct influence on both (thermo-)mechanical (ultimate failure, density, thermal expansion, stability range) and chemical (refractoriness, chemical inertia) properties through the crystalline structure.

For short term applications, it is sometimes possible to “trick” nature but chemistry becomes a key factor when composites are designed for longer service time. More expansive materials can then be considered and will become necessary when future requirements to reduce engines pollution will impose higher working temperatures and a reduction of the air flows used to cool down metallic parts, making the search for a good compromise between physical (mechanical) and chemical (service time) criteria [68] all the more important. In this context, work on long-term durability in corrosive atmosphere is gaining interest [69-74].

Among the most promising leads are Functionally Graded Materials (FGM) [35,75], hierarchical composites (double reinforcement with fibers and particulates [75] and/or control of the interphases [76]) and nature imitation [77].

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